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I, KAY WARD, TEAM LEADER EXAMINATION SUPPORT AND SALES
hereby certify that annexed is a true copy of the Provisional specification in
connection with Application No. PQ 2234 for a patent by CERAMIC FUEL
CELLS LIMITED filed on 16 August 1999.

WITNESS my hand this
Twenty-eighth day of August 2000

KAY WARD
TEAM LEADER EXAMINATION
SUPPORT AND SALES

Ceramic Fuel Cells Limited

AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Fuel Cell System"

The invention is described in the following statement:

FUEL CELL SYSTEM

The present invention relates to fuel cells and is particularly concerned with the fuel supply to a fuel cell electrical power generating system.

5

Fuel cells convert gaseous fuels (such as hydrogen, natural gas and gasified coal) via an electrochemical process directly into electricity. A fuel cell continuously produces power when supplied with fuel and oxidant, normally air. A typical fuel cell consists of an electrolyte (ionic conductor, H^+, O^{2-}, CO_3^{2-} etc.) in contact with two electrodes (mainly electronic conductors). On
10 shorting the cell through an external load, fuel oxidises at the anode resulting in the release of electrons which flow through the external load and reduce oxygen at the cathode. The charge flow in the external circuit is balanced by ionic current flows within the electrolyte. Thus, at the cathode oxygen from the air or other oxidant is dissociated and converted to oxygen ions which migrate through the electrolyte membrane and react with the fuel at the anode/electrolyte interface. The
15 voltage from a single cell under load conditions is in the vicinity of 0.6 to 1.0 V DC and current densities in the range 100 to 1000 mAcm^{-2} can be achieved.

Several different types of fuel cells have been proposed. Amongst these, the solid oxide fuel cell (SOFC) is regarded as the most efficient and versatile power generation system, in particular for
20 dispersed power generation, with low pollution, high efficiency, high power density and fuel flexibility. SOFC's operate at elevated temperatures, for example 800 - 1000°C. Other fuel cells which operate at elevated temperatures include the molten carbonate fuel cell requiring a minimum temperature of 650°C. However, SOFC's are the primary interest for the invention and further discussion herein will be mainly directed to these without intending to be limited in any way.
25

Numerous SOFC configurations are under development, including the tubular, the monolithic and the planar design. The planar or flat plate design is the most widely investigated. Single planar SOFC's are connected via interconnects or separators to form multi-cell units, sometimes termed fuel cell stacks. Gas flow paths are provided between the interconnects and respective electrodes.
30 In this concept the components - electrolyte/electrode laminates and interconnect plates, which may have gas channels formed therein - are fabricated individually and then stacked together. With this

arrangement, external and internal co-flow, counter-flow and cross-flow manifolding options are possible for the gaseous fuel and oxidant.

Traditionally hydrogen, usually moistened with steam, has been used as a fuel cell fuel. However,
5   in order to be economically viable the fuel must be as cheap as possible. One relatively cheap source of hydrogen is natural gas, primarily methane with a very small proportion of heavy hydrocarbons (C_2+). Natural gas is commonly converted to hydrogen in a steam reforming reaction, but the reaction is endothermic and, because of the stability of methane, requires a reforming temperature of at least about 650°C for substantial conversion. Thus, hydrogen produced by steam reforming
10 natural gas may not be a cheap source of fuel. While high temperature fuel cell systems produce heat which must be removed, heat exchangers capable of transferring thermal energy at the required level of at least about 650°C from the fuel cells to a steam reformer are expensive. For complete steam reforming of methane, the literature suggests a minimum temperature of 800°C is required.

15 It has been proposed to alleviate this problem by using natural gas as a fuel source for a high temperature planar fuel cell stack and subjecting the natural gas to steam reforming within the stack, at a temperature of at least about 650°C, using catalytically active anodes. However, given the endothermic nature of the methane steam reforming reaction, too much methane in the fuel stream can lead to excessive cooling of the fuel cell stack. To alleviate this problem the fuel stream has
20 been restricted to a maximum of about 25% methane with the natural gas being subjected to partial steam pre-reforming at elevated temperatures approaching 700°C upstream of the fuel cell stack.

It would be highly advantageous to the economics of producing electricity in a fuel cell to be able to use other sources of fuel, including liquid fuels such as higher hydrocarbons, and to be able to
25 reduce the temperature of any process for pre-reforming the fuel source to well below 650°C.

According to the present invention there is provided a process for producing electricity in a fuel cell which comprises reforming higher carbon (C_{3+}) hydrocarbon fuels in a steam pre-reformer at a temperature of no greater than 500°C to produce a fuel stream including methane and hydrogen,
30 and supplying the fuel stream and an oxidant to a high temperature fuel cell in which the methane is reformed and electricity is produced by reacting the fuel stream at an anode of the fuel cell and

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reacting the oxidant at a cathode of the fuel cell.

By the present invention, a substantially wider source of fuel may be used for the fuel cell, including liquid higher hydrocarbons such as LPG, petrol (gasoline) and diesel, while a lower
5 temperature of no greater than 500°C may be used for steam reforming the higher hydrocarbon fuel source since there is no requirement to reform any methane in the steam pre-reformer. This permits a relatively small pre-reformer reactor to be used which, combined with the reduced maximum operating temperature of 500°C, enables a simplified and therefore cheaper pre-reformer system to be adopted.
10

While some reforming of methane is likely to occur in the steam pre-reformer, even at the low temperatures proposed, it is emphasised that this is not necessary to the invention. Generally the methane content of the fuel stream will be at least 25% by volume with the potential that excessive cooling of the fuel cell may be encountered as a result of the endothermic methane internal steam
15 reforming reaction. This problem is particularly likely to be encountered in a wholly ceramic SOFC fuel cell stack due to the low thermal conductivity of ceramic materials, but can be alleviated by incorporating metal or metallic components in the fuel cell stack, for example as the gas separators between individual fuel cells, to improve the thermal conductivity across the stack. Alternatively, other means may be provided to prevent excessive cooling at the fuel entry edge of each fuel cell
20 assembly.

Steam reforming of the higher hydrocarbon fuel source is preferably performed at a temperature no greater than about 450°C, more preferably in a range of about 250 to 450°C, most preferably in a range of about 300 to 400°C.
25

By way of example, at 300 to 400°C propane, C_3H_8, the principal component of LPG, may be steam reformed to CH_4, CO, CO_2 and H_2. The CH_4 in this fuel stream is then internally reformed within the fuel cell in the presence of steam during the oxidation reaction at the anode to produce a waste stream of CO_2 and H_2O. The temperature in the fuel cell should be at least 700°C to ensure
30 substantially complete reforming of the methane. In an SOFC the temperature is likely to be at least 800°C so that complete reforming of the methane is likely to be achieved.

Advantageously, waste heat from the fuel cell is recycled to the steam pre-reformer, which is preferably operated adiabatically. Since the pre-reformer is only required to operate at a maximum temperature of 500°C, any heat exchanger transferring the waste heat to the reformer may be of
5 relatively simple construction and formed of relatively low-cost materials.

A variety of different steam reformers have been proposed and any of these may be adopted for the pre-reformer, bearing in mind the maximum operating temperature of 500°C.

10 Preferably, the anode in the fuel cell comprises a nickel material which is used to catalyse the reforming reaction in the fuel cell. The fuel cell and its associated assembly can take any suitable form provided it operates at a temperature of at least 650°C to provide at least substantial conversion of the methane in the internal reforming reaction. By way of example only, several different planar SOFC systems, SOFCs and materials are described in our International Patent
15 Application PCT/AU96/00140, PCT/AU96/00594, PCT/AU98/00437, PCT/AU98/00719 and PCT/AU98/00956, the contents of which are incorporated herein by reference.

Commonly, steam reforming of hydrocarbons is carried out at a steam to carbon (S/C) ratio of greater than 2. In the present invention, this however would result in significant dilution of the fuel
20 with steam and thus reduction in the fuel value. For example, for butane (C_4H_{10}), eight volume parts of steam must be added to one volume part of fuel for an S/C ratio of 2. For diesel (C_{10}), twenty parts of steam must be added to one part of fuel to achieve an S/C ratio of 2, with the result that it is virtually pure steam, leading to inefficient electricity production. Preferably therefore, the S/C ratio in the pre-reformer is below 1.5, more preferably below 1.25 and most preferably below 1.
25
Potential carbon deposition problems at the proposed low steam to carbon ratios are alleviated by the mild conditions (temperature no greater than 500°C) used in the pre-reformer. If pre-reforming is carried out at very low steam to carbon ratios, additional steam may be introduced to the fuel stream entering the fuel cell. Advantageously, the addition of steam may be provided by recycling
30 some of the anode exhaust stream.

The advantages of a relatively low S/C ratio and a relatively low temperature in the pre-reformer

may be seen from the thermodynamic equilibrium molar compositions of LPG and gasoline reformed at the identified inlet temperatures given in the following tables in which S/C is the steam to hydrocarbon carbon ratio. For example S/C equals 1.0 is equivalent to 3.15 moles of steam for every mole of LPG or to 7.93 moles of steam for every mole of gasoline.

5

Molar Compositions of Reformed LPG (Assumed to be 85% propane and 15% butane)

10

Temp.	200°C					250°C				
S/C	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
CH_4	0.7133	0.4965	0.3807	0.3085	0.2591	0.7091	0.4909	0.3749	0.3028	0.2536
C_2^+	4.0E-06	1.1E-06	5.7E-07	2.4E-08	3.1E-12	6.9E-06	1.9E-06	9.8E-07	8.8E-08	3.1E-12
H_2O	0.1347	0.3923	0.5306	0.6169	0.6759	0.1310	0.3845	0.5206	0.6057	0.6637
H_2	0.0041	0.0069	0.0080	0.0086	0.0090	0.0107	0.0182	0.0210	0.0224	0.0234
CO	3.2E-05	1.3E-05	8.9E-06	6.6E-06	5.3E-06	0.0002	8.7E-05	5.8E-05	4.4E-05	3.6E-05
CO_2	0.1479	0.1042	0.0807	0.0660	0.0560	0.1490	0.1064	0.0834	0.0690	0.0592
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

15

20

Temp.	300°C					350°C				
S/C	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
CH_4	0.7007	0.4797	0.3635	0.2918	0.2430	0.6855	0.4606	0.3448	0.2738	0.2258
C_2^+	1.1E-05	3.0E-06	1.5E-06	9.1E-07	3.1E-12	1.6E-05	4.3E-06	2.1E-06	1.3E-06	3.0E-12
H_2O	0.1239	0.3691	0.5013	0.5839	0.6405	0.1127	0.3437	0.4694	0.5486	0.6031
H_2	0.0238	0.0403	0.0463	0.0493	0.0510	0.0458	0.0772	0.0880	0.0930	0.0956
CO	0.0010	0.0004	0.0003	0.0002	0.0002	0.0040	0.0017	0.0012	0.0009	0.0008
CO_2	0.1506	0.1105	0.0886	0.0748	0.0653	0.1520	0.1168	0.0966	0.0837	0.0747
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

25

30

Temp.	400°C					450°C				
S/C	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
CH_4	0.6602	0.4318	0.3172	0.2478	0.2013	0.6196	0.3919	0.2804	0.2139	0.1699
C_2^+	2.3E-05	5.8E-06	2.8E-06	1.6E-06	2.9E-12	2.9E-05	7.2E-06	3.3E-06	2.8E-12	2.8E-12
H_2O	0.0981	0.3076	0.4243	0.4989	0.5510	0.0824	0.2627	0.3683	0.4375	0.4869
H_2	0.0783	0.1307	0.1475	0.1547	0.1579	0.1228	0.1995	0.2229	0.2318	0.2349
CO	0.0131	0.0058	0.0041	0.0032	0.0027	0.0352	0.0166	0.0119	0.0096	0.0082
CO_2	0.1503	0.1242	0.1069	0.0954	0.0871	0.1399	0.1292	0.1165	0.1072	0.1001
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Temp.	500°C					550°C				
S/C	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
CH_4	0.5584	0.3395	0.2343	0.1727	0.1325	0.4784	0.2744	0.1797	0.1257	0.0913
C_2^+	3.3E-05	7.9E-06	3.4E-06	1.8E-06	2.6E-12	3.3E-05	7.5E-06	2.9E-06	1.4E-06	2.4E-12
H_2O	0.0671	0.2137	0.3062	0.3698	0.4171	0.0511	0.1652	0.2446	0.3031	0.3492
H_2	0.1816	0.2802	0.3091	0.3186	0.3203	0.2544	0.3680	0.3993	0.4070	0.4053
CO	0.0772	0.0407	0.0300	0.0243	0.0207	0.1361	0.0832	0.0632	0.0517	0.0438
CO_2	0.1157	0.1259	0.1204	0.1146	0.1094	0.0800	0.1092	0.1132	0.1125	0.1103
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Temp.	600°C					700°C			
S/C	0.5	1.0	1.5	2.0	2.5	1.0	1.5	2.0	2.5
CH_4	0.3942	0.2018	0.1211	0.0776	0.0515	0.0825	0.0314	0.0142	0.0072
C_2^+	3.1E-05	5.9E-06	2.0E-06	2.3E-12	2.3E-12	2.0E-06	3.5E-12	2.0E-12	2.1E-12
H_2O	0.0334	0.1206	0.1896	0.2455	0.2932	0.0533	0.1185	0.1845	0.2456
H_2	0.3318	0.4563	0.4850	0.4869	0.4778	0.5955	0.6031	0.5773	0.5438
CO	0.1970	0.1401	0.1100	0.0902	0.0756	0.2395	0.1949	0.1561	0.1260
CO_2	0.0435	0.0812	0.0943	0.0997	0.1018	0.02925	0.0521	0.0679	0.0774
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Temp.	700°C (cont.)		750°C					
S/C	3.0	3.5	1.0	1.5	2.0	2.5	3.0	3.5
CH_4	0.0040	0.0023	0.0486	0.0118	0.0045	0.0021	0.0011	0.0007
C_2^+	2.2E-12	2.2E-12	1.4E-11	1.9E-12	2.0E-12	2.1E-12	2.2E-12	2.2E-12
H_2O	0.3005	0.3492	0.0331	0.1054	0.1798	0.2459	0.3033	0.3533
H_2	0.5099	0.4781	0.6362	0.6265	0.5865	0.5456	0.5083	0.4746
CO	0.1030	0.0855	0.2666	0.2158	0.1708	0.1374	0.1125	0.0937
CO_2	0.0826	0.0849	0.0155	0.0405	0.0584	0.0690	0.0748	0.0777
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Molar Compositions of Reformed Gasoline (Assumes 93% C_8H_{18} n-Octane and 7% C_6H_{12}: CH_2 (Anti-Knock Agent))

Temp.	200°C					250°C				
S/C	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
CH_4	0.7361	0.5000	0.3786	0.3046	0.2548	0.7320	0.4919	0.3701	0.2962	0.2466
C_2^+	7.2E-06	1.3E-06	4.9E-07	3.4E-07	1.4E-07	1.3E-05	2.2E-06	1.0E-06	3.2E-12	3.2E-12
H_2O	0.0554	0.3584	0.5142	0.6092	0.6731	0.0523	0.3476	0.4998	0.5925	0.6550
H_2	5.5E-11	5.1E-11	5.0E-11	4.9E-11	4.8E-11	0.0063	0.0160	0.0191	0.0207	0.0217
CO	6.5E-05	1.7E-05	1.2E-05	8.3E-06	7.1E-06	0.0004	0.0001	7.3E-05	5.5E-05	4.4E-05
CO_2	0.2084	0.1416	0.1072	0.0862	0.0721	0.2090	0.1444	0.1109	0.095	0.0767
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Temp.	300°C					350°C				
S/C	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
CH_4	0.7262	0.4819	0.3598	0.2861	0.2367	0.7144	0.4644	0.3422	0.2691	0.2204
C_2^+	2.0E-05	3.4E-06	1.6E-06	9.5E-07	3.1E-12	3.0E-05	4.9E-06	2.3E-06	1.3E-06	3.1E-12
H_2O	0.0491	0.3343	0.4822	0.5724	0.6333	0.0449	0.3122	0.4530	0.5393	0.5978
H_2	0.0139	0.0357	0.0424	0.0457	0.0476	0.0271	0.0690	0.0814	0.0871	0.0902
CO	0.0021	0.0006	0.0004	0.0003	0.0002	0.0081	0.0022	0.0014	0.0011	0.0009
CO_2	0.2087	0.1475	0.1152	0.0955	0.0822	0.2055	0.1522	0.1220	0.1034	0.0907
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Temp.	400°C					450°C				
S/C	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
CH_4	0.6911	0.4374	0.3158	0.2441	0.1968	0.6486	0.3986	0.2800	0.2111	0.1661
C_2^+	4.0E-05	6.6E-06	2.9E-06	1.7E-06	3.0E-12	4.8E-05	8.1E-06	3.5E-06	1.9E-06	1.1E-06
H_2O	0.0415	0.2805	0.4109	0.4921	0.5477	0.0399	0.2409	0.3579	0.4328	0.4855
H_2	0.0483	0.1181	0.1380	0.1465	0.1505	0.0824	0.1826	0.2108	0.2218	0.2260
CO	0.0247	0.0072	0.0048	0.0037	0.0031	0.0592	0.0202	0.0137	0.0107	0.0089
CO_2	0.1944	0.1568	0.1305	0.1136	0.1019	0.1699	0.1577	0.1376	0.1236	0.1135
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Temp.	500°C					550°C				
S/C	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
CH_4	0.5830	0.3461	0.2342	0.1703	0.1293	0.4996	0.2794	0.1793	0.1234	0.0885
C_2^+	4.9E-05	8.9E-06	3.6E-06	1.8E-06	1.0E-06	4.5E-05	8.3E-06	3.1E-06	1.4E-06	7.3E-07
H_2O	0.0382	0.1975	0.2989	0.3671	0.4170	0.0329	0.1544	0.2402	0.3023	0.3507
H_2	0.1342	0.2597	0.2951	0.3072	0.3104	0.2032	0.3455	0.3842	0.3949	0.3944
CO	0.1135	0.0481	0.0336	0.0266	0.0222	0.1793	0.0957	0.0694	0.0554	0.0462
CO_2	0.1311	0.1486	0.1382	0.1288	0.1211	0.0849	0.1250	0.1269	0.1240	0.1202
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Temp.	600°C					700°C			
S/C	0.5	1.0	1.5	2.0	2.5	1.0	1.5	2.0	2.5
CH_4	0.4156	0.2048	0.1201	0.0755	0.0492	0.0831	0.0302	0.0133	0.0066
C_2^+	4.1E-05	6.3E-06	2.0E-06	7.9E-07	2.3E-12	2.1E-06	9.1E-12	2.1E-12	2.2E-12
H_2O	0.0227	0.1142	0.1875	0.2464	0.2962	0.0515	0.1197	0.1886	0.2520
H_2	0.2776	0.4336	0.4696	0.4740	0.4659	0.5744	0.5872	0.5620	0.5286
CO	0.2409	0.1568	0.1188	0.0954	0.0788	0.2594	0.2058	0.1621	0.1291
CO_2	0.0432	0.0906	0.1040	0.1087	0.1099	0.0316	0.0571	0.0740	0.0837
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Temp.	700°C (cont.)		750°C					
S/C	3.0	3.5	1.0	1.5	2.0	2.5	3.0	3.5
CH_4	0.0036	0.0021	0.0488	0.0112	0.0042	0.0019	0.0010	0.0006
C_2^+	2.2E-12	2.3E-12	1.1E-06	1.3E-10	2.0E-12	2.1E-12	2.2E-12	2.3E-12
H_2O	0.3085	0.3583	0.0322	0.1078	0.1851	0.2532	0.3120	0.3630
H_2	0.4947	0.4629	0.6157	0.6095	0.5699	0.5294	0.4922	0.4588
CO	0.1045	0.0861	0.2866	0.2268	0.1768	0.1406	0.1142	0.0944
CO_2	0.0887	0.0906	0.0167	0.0447	0.0640	0.0749	0.0806	0.0832
Total	1.0000	1.0000	1.0000	1.0000	1.00000	1.0000	1.0000	1.0000

As may be seen, the level of methane in the pre-reformed fuel decreases with increasing reforming temperature and increasing steam to carbon ratio.

One embodiment of a process in accordance with the invention is now illustrated by way of example only with reference to the accompanying drawing which is a block diagram of the process illustrating a typical steam pre-reformer and an SOFC stack.

In one example, propane was subjected to steam reforming using a commercially available catalyst at 378°C and at 328°C using a variety of space velocities and S/C ratios. The catalyst was a pre-reformer catalyst C11 - PR supplied by United Catalysts Corporation. The space velocities for the total gas flow ranged between 25,000 and 70,000 hr^{-1} and for propane ranged between 10,000 and

20,000 hr^{-1}. The measured conversions given in the following table illustrate that the results predicted by the thermodynamic calculations given above can be at least approached. The steam reforming was conducted in a microreactor system with on-line analysis of the gas compositions. It is to be noted that the experimental set-up was not ideal, and it is believed that this accounts for

5 the incomplete conversions.

Temp (°C)	Steam/Carbon ratio	Steam/Gas	%H_2	%CO	%CH_4	%CO_2	%C_3H_8	Conversion of Propane
378	1.37	4.11	34	2.4	48.9	14.2	0.6	97.5
328	1.37	4.11	15.4	2	62.7	15	4.8	84.6
328	1.01	3.03	24.4	3.8	56.5	12.4	3	89.2
328	0.75	2.25	21.4	1.6	61.1	13.1	3.1	89.0
328	0.5	1.5	17.3	1.6	64.6	12.9	3.6	88.2

15 Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said

20 steps, features, compositions and compounds.

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CERAMIC FUEL CELLS LIMITED

30 By Its Patent Attorneys

DAVIES COLLISON CAVE